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HIGH TEMPERATURE OXIDATION OF METALS, ALLOYS AND CERAMIC CARBIDES AND BORIDES

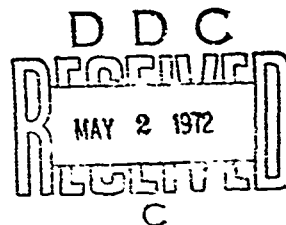
HENRY C. GRAHAM

METALLURGICAL AND CERAMICS RESEARCH LABORATORY

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AEROSPACE RESEARCH LABORATORIES
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report is based on research conducted between July 1966 and September 1971 by the Metallurgy and Ceramics Research Laboratory, Aerospace Research Laboratories, Wright-Patterson AFB, Ohio. Principal investigator was D. Henry C. Graham, with the participation of Captain H. Davis and Major G. Uhlig. The effort has been documented under Project 7021, "Structure and Properties of Solids", In-House Work Unit 22, "High Temperature Oxidation of Metals, Alloys and Ceramic Carbides and Borides", and this document constitutes the final report for Work Unit 7021-60-22.

ABSTRACT

A knowledge of high temperature oxidation mechanisms is fundamental to the design or improvement of vehicle materials which resist extreme oxidizing environments. The oxidation behavior of several Ni-base alloys was studied to 1200°C. ZrB₂ and ZrB₂+SiC oxidation was studied to 2000°C. Of particular importance in these studies were the determination of the oxidation reaction kinetics by continuous weight change measurements as a function of temperature and oxygen partial pressure. The major accomplishments of the research effort are summarized and the publications generated under this program are listed.

The object of this work unit was the study of the high temperature oxidation behavior of metals, alloys and ceramic carbides and borides. Primarily through the use of detailed kinetic and microstructural studies the fundamental oxidation mechanisms were determined. In some cases it was necessary to determine the fundamental thermodynamic behavior of the materials or the oxidation products before a detailed analysis could be completed. Materials studied were ZrB_2 ; $\text{ZrB}_2\text{-20SiC}$; $\text{ZrB}_2\text{-18SiC-10C}$; $\text{Ni-10 to 30 Cr-1 ThO}_2$; Ni-20Cr-2 ThO_2 ; Ni-9 Cr-6 Al ; and Ni-9 Cr-6 Al-0.1Y . The kinetic measurements were performed on several continuous weighing microbalance systems under closely controlled conditions of temperature, oxygen partial pressure, total pressure and flow rate. The effects of sample preparation, sample introduction method or sequence and of pretreatment were examined for most systems. Normal operating temperatures were in the range 900-1500 C with oxygen partial pressure of 0.001 atm, total pressures usually about 0.1 atm. and flow rates of the order of 150 cc/min at 1 atm. Some exploratory measurements were made to determine the feasibility of making thermogravimetric measurements at temperatures as high as 2000 C. Initial work on this program was involved in determining the kinetics of the oxidation of zirconium diboride materials. The sample materials were obtained from Manlabs, Inc. through John Fenter of the Air Force Materials Laboratory. Although Manlabs and some of their subcontractors had characterized the diborides under Air Force contract, these studies were of an engineering nature, designed primarily to obtain data, and were not suitable for determining fundamental oxidation mechanisms. For example, the Manlabs work hypothesized that the change in behavior for these materials in the vicinity of 1100°C was related to the monoclinic to tetragonal phase transformation of the "protective" ZrO_2 scale. The data determined on this work unit clearly show that the change is caused by the increased loss of the protective B_2O_3 liquid layer and further that the ZrO_2 is porous and therefore not protective. Other results on this work unit also showed that the behavior between 1100° and 1500°C was related to the presence or absence of the protective silica-rich layer. In completing this work, the dependencies on temperature, time, oxygen partial pressure, total pressure and water partial pressure were clearly defined for the nominally pure diboride and the diboride containing silicon carbide additions. The work on the carbon-rich diboride was suspended since the material was inhomogeneous and therefore not capable of giving reproducible, quantitative data.

Early in the diboride work a facility to make continuous thermogravimetric measurements up to 2000°C in an oxidizing environment was constructed. The facility functioned well but no materials could be found to suspend the diboride at these temperatures. In all cases (various noble metals and ceramics were tried) the reaction products immediately reacted with the suspension and the sample would fall to the bottom of the furnace. It is probable that high temperature measurements could be made on these materials if the samples were allowed to come to temperature slowly and/or were allowed to pre-oxidize. Manlab's furnace measurements were carried out in this manner and the extent of interaction between the setter material and the diborides was minor.

In our superalloy program, the first alloys studied were a set of three thoriated nickel-chromium alloys with varying chromium contents which were fabricated by Sherritt-Gordon, Inc. for a creep study at Battelle Memorial Institute in Columbus, Ohio. Some of each of these alloys were given to ARL by Dr. Ben Wilcox of Battelle, who was the principal investigator on the creep study. The alloys were nominally Ni-10, 20 & 30 Cr-1%ThO₂. It was soon apparent that the lowest Cr alloy would form either NiO or Cr₂O₃ as the predominant oxide scale, depending upon variations such as surface preparation. This alloy was used to study the formation of these two oxides under similar conditions and thereby proved to be quite enlightening with respect to determining the oxidation mechanism. Probably the most significant result, as related to a particular alloy, was that the presence of ThO₂ did reduce the oxidation rate of the Cr₂O₃ formers by an order of magnitude. Several possible hypotheses have been given for this behavior and further work will be carried on under a new work unit to clearly establish the mechanism.

During this study, it was found that at 1000°C and above in oxidizing environments the Cr₂O₃ scale was being lost. A study of the behavior of Cr₂O₃ followed and led to a publication on the subject. While many investigators had guessed or hinted at the loss mechanism, this work proved that Cr₂O₃ was oxidizing to CrO₃ which was subsequently vaporizing. Additionally, it showed that the vaporization rate was dependent on a boundary layer developed at the surface and thereby controlled by the gas dynamics.

A system for measuring the contributions to weight loss made by condensible vapor species was used in this study. It had been developed to measure the loss of B₂O₃ from the diborides and was here again shown to be quite valuable. The technique consists of suspending a ceramic crucible around and above the sample. Since the top, closed portion of the crucible is considerably cooler than the sample, the vapor species condense on it and therefore do not contribute to a weight loss. This

method allows the total oxygen consumption to be measured since both the solid and gaseous oxidation products are collected and weighed, i. e., the only weight change is the oxygen added to form both types of products. Other systems studied were the alumina forming super-alloys with and without yttrium additions. This work, primarily accomplished by visiting scientist Dr. Ingard Kvernes, was initially centered around the development of the Ni-9Cr-6Al alloy and later extended to the effect of very small yttrium additions. The alloy development work was under an AFML contract, with the determination of the nature of the yttrium effect to be accomplished at ARL. The most interesting result of this study was that yttrium additions led to a finer oxide scale which was very adherent in direct contrast to scales formed on the Ni-9Cr-6Al alloy. This effect is unexplained at this time and like the ThO_2 effect will be a part of a new work unit.

Very recently some studies were initiated to determine the effect of Na_2SO_4 on the oxidation behavior of materials. This technique of studying "hot corrosion" was adopted after considerable literature study as well as communication with active workers and users interested in hot corrosion. While certainly not reproducing hot corrosion conditions in an airborne gas turbine, it is felt that this is the best method presently available for the study of accelerated attack due to Na_2SO_4 in a quantitatively controlled manner. The initial work has been on commercial Td Ni-Cr and the results are still preliminary in nature.

As a result of this work, the thoria dispersion work, the yttrium work and the projected movement of the oxidation group into several other new areas, this work unit is being closed out and three new in-house research plans are being initiated to more closely reflect the objectives of each study and their interactions with other Metallurgy and Ceramics Research Laboratory programs.

The following is a list of publications to date on this work unit. Additional publications, primarily concerned with Ni-Cr-Al and Ni-Cr-Al-Y, are in preparation.

H. G. Graham and W. C. Tripp, "Induction Heated High Temperature Balance System", Vacuum Microbalance Techniques, Vol. 6, Plenum Press (1967)

W. C. Tripp, R. W. Vest and H. C. Graham, "Use of a Microthermometer in Determining the Defect Structure of Metal Oxides, " Vacuum Microbalance Techniques, Vol. 6, Plenum Press (1967)

H. C. Graham and W. C. Tripp, "Oxidation Study of Zirconium Diboride with Various Additives," Proceedings of the 34th Meeting of the Propulsion and Energetics Panel of AGARD, October (1969)

H. C. Graham, W. C. Tripp and H. H. Davis, "Microbalance Techniques Associated with Oxidation Studies," Vacuum Microbalance Techniques, Vol. 9, Plenum Press (1970)

H. H. Davis and H. C. Graham "Oxidation/Vaporization Kinetics of Cr_2O_3 ," J. Am. Ceram. Soc., 54, (2) 89 (1971)

W. C. Tripp and H. C. Graham, "Thermogravimetric Study of the Oxidation of ZrB_2 in the Temperature Range 800° to 1500°C ," J. Electro Chem. Soc., 118 (7) 1195 (1971)

H. H. Davis, H. C. Graham and I. Kvernes, "Oxidation of Ni-Cr-1% ThO_2 Alloys at 1000° and 1200°C ," Oxidation of Metals, 3 (5) (1971)

W. C. Tripp, H. H. Davis and H. C. Graham, "Microstructural Features of Oxide Scales Formed on Zirconium Diboride Materials", Materials Science Research - Ceramics in Severe Environments, Vol. 6, Plenum Press (1971)

H. C. Graham and W. C. Tripp, "Separation of Contributions to Weight Change of Volatile and Non-Volatile Products During High Temperature Oxidation Measurements", Air Force Research Review, Number 1, July-August (1970)

Rayleigh intensity, converge to the cusps. A study of the requisite Rayleigh optical depth is made in Paper XVI.

Besides the cusp effect, the ultraviolet polarization is variable over the disk, lacking symmetry about the equator. Any close correlation between the ultraviolet cloud and polarization patterns was neither affirmed nor denied by a comparison made on 21 June 1967. Simultaneous photography and polarimetry were done then, but no detailed comparison is possible for several reasons, particularly the limited polarization coverage of the disk and the variations of differential refraction and effective wavelength with zenith distance. No contradiction of the reciprocity principle was indicated by the polarimetry at longer wavelengths, though it certainly fails in the ultraviolet (the principle is discussed by Minnaert 1941; and Chandrasekhar 1947).

No large anomalies in the polarization position angle were found, although a small but consistent effect is that for the intermediate limb regions Nos. 6 and 7 (Fig. 7) the position angle is more nearly parallel to the limb than is the position angle for the integrated disk. This is true for each of the 12 observations of one or the other of these two regions made in May and June 1967, regardless of wavelength. The amounts of this rotation range from 0.7 to 14° , with a mean of 5° .

Perhaps the simplest explanation of this rotation is achieved by considering polarization by second-order scatterings, which would be particularly important along the limb. For the photons reaching the observer there is a preference for the plane of secondary scattering to be tangential to the limb. Photons initially scattered upward have a lower probability of further scattering, while photons scattered downward have an enhanced probability of absorption. A secondary scatterer sees a bright horizon and a darker zenith and nadir. So if all second scatterings are assumed to occur in a negatively polarizing aerosol (the molecular optical depth above the clouds cannot be large—see Paper XVI), the consequent electric-vector vibration will be in the plane of secondary scattering, and therefore tangential to the limb. The combination of this polarization with either positive or negative polarization by single scattering will result in a principal electric vector more nearly parallel to the limb than that of the single scattering.

The very pronounced tangentially polarized component observed by Dollfus (1966) in both red and green at a phase angle of 170° may have a similar explanation. The above qualitative discussion must,

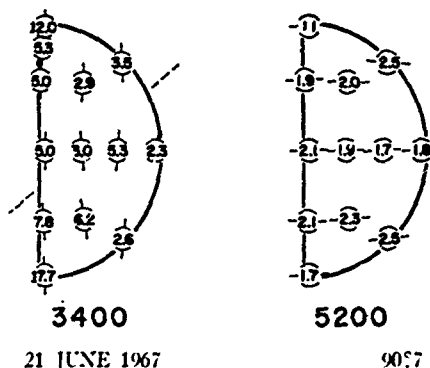


FIG. 8. Regional polarization at 91° phase angle. The regions are numbered in Fig. 7.

of course, await polarization radiative-transfer calculations for any quantitative comparisons.

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